This Page Is Inserted by IFW Operations
and is not a part of the Official Record

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

IMAGES ARE BEST AVAILABLE COPY.

As rescanning documents *will not* correct images, please do not report the images to the Image Problem Mailbox.

⑲ 日本国特許庁（JP）　　⑪ 特許出願公開

⑫ 公開特許公報（A）　　昭57―22043

⑮Int. Cl.^{3}	識別記号	庁内整理番号
B 32 B　1/08		6358―4 F
B 29 D　3/02	207	7224―4 F
//B 32 B　5/02		7603―4 F

㊸公開　昭和57年(1982) 2月4日

発明の数　2
審査請求　未請求

（全 4 頁）

---

(54)繊維強化熱硬化性樹脂製筒状体及びその製造方法

㉑特　　願　昭55―95716
㉒出　　願　昭55(1980) 7月15日
㊷発 明 者　尾崎行功
　　　　　　明石市鳥羽字沢野1974―202番地
㊷発 明 者　谷口紫郎
　　　　　　吹田市末広町8―32
㊷発 明 者　鉛谷和男
　　　　　　奈良市敷島町2丁目498―1番地
㊶出 願 人　日本触媒化学工業株式会社
　　　　　　大阪市東区高麗橋5丁目1番地
㊹代 理 人　山口剛男

明　細　書

1. 発明の名称

繊維強化熱硬化性樹脂製筒状体及びその製造方法

2. 特許請求の範囲

1. 熱硬化性樹脂と補強用繊維とを用いて繊維強化熱硬化性樹脂筒状物を成形したのち該筒状物の母線方向に一条又は複数条切断して、成形時に付与された曲率を変えることが可能な樹脂板とし、次いで該樹脂板の端部同士を接合して成る繊維強化熱硬化性樹脂製筒状体。

2. 熱硬化性樹脂が不飽和ポリエステル樹脂である特許請求の範囲第1項記載の繊維強化熱硬化性樹脂製筒状体。

3. 補強用繊維がガラス繊維である特許請求の範囲第1項記載の繊維強化熱硬化性樹脂製筒状体。

4. 熱硬化性樹脂と補強用繊維とを用いて繊維強化熱硬化性樹脂筒状物を成形したのち該筒状物の母線方向に一条又は複数条切断して、成形時に付与された曲率を変えることが可能な樹脂板とし、次いで該樹脂板の切断端部同士を接合することを特徴とする繊維強化熱硬化性樹脂製筒状体の製造方法。

5. 熱硬化性樹脂が不飽和ポリエステル樹脂である特許請求の範囲第4項記載の繊維強化熱硬化性樹脂製筒状体。

6. 補強用繊維がガラス繊維である特許請求の範囲第4項記載の繊維強化熱硬化性樹脂製筒状体。

3. 発明の詳細な説明

本発明は繊維強化熱硬化性樹脂製筒状体及びその製造方法に関するものである。詳しくは強度及び耐薬品性に優れ、輸送に便利な繊維強化熱硬化性樹脂製筒状体及びその製造方法に関するものである。

従来、繊維強化熱硬化性樹脂（以下、FRPと記す。）は、強度や耐薬品性に優れ、薬品タンク、水槽、サイロ等に広く用いられて

いる。これらのＦＲＰ製の製品は１基当りの重量が鋼製やコンクリート製等の製品に較べて軽量で輸送に有利であるものの、占める容積は鋼製やコンクリート製とあまり変わらず、輸送手段が最も効率良く活用されているとは言い難い。容積が大きくて輸送困難な大型のＦＲＰ製タンクは、タンク壁面を縦横に細かく分割した形状のＦＲＰ製のパネルをあらかじめ成形し、これをボルト、鋲等で接合してタンクに組立てる方法が知られているが、この方法では分割したＦＲＰ製パネルの形状をタンクの形状に応じて個々に決めることが必要であり、従つてタンクの形状の種類だけパネルの成形型を必要とし、多大な設備費を要するという欠点がある。

本発明の目的は、強度及び耐薬品性に優れ輸送にも便利な、タンクやサイロ等の円筒型や角型のＦＲＰ製筒状体を提供するものである。本発明の他の目的は、このようなＦＲＰ製筒状体を製造する方法を提供するものである。

即ち第１の発明は、熱硬化性樹脂と補強用繊維とを用いてＦＲＰ筒状物を成形したのち該筒状物の母線方向に一条又は複数条切断して、成形時に付与された曲率を変えることが可能なＦＲＰ板とし、次いで該ＦＲＰ板の切断端部同士を接合して成るＦＲＰ製筒状体に関するものである。

また第２の発明は、熱硬化性樹脂と補強用繊維とを用いてＦＲＰ筒状物を成形したのち該筒状物の母線方向に一条又は複数条切断して、成形時に付与された曲率を変えることが可能なＦＲＰ板とし、次いで該ＦＲＰ板の切断端部同士を接合することを特徴とするＦＲＰ製筒状体の製造方法に関するものである。

本発明で用いられる熱硬化性樹脂としては、不飽和ポリエステル樹脂、エポキシ樹脂、ビニルエステル樹脂等を用いることができるが、中でも不飽和ポリエステル樹脂が好ましい。

補強用繊維としては、ガラス繊維、ポリアミド繊維、炭素繊維等当技術分野で公知のものを用いることができるが、中でもガラス繊維が好ましい。

熱硬化性樹脂と補強用繊維とを用いてＦＲＰ筒状物を成形するには、フイラメントワインデイング法、手積法、スプレーアップ法等従来公知の方法が用いられ、その必要とする仕上り外観、強度、耐水性等により適宜選択される。そしてＦＲＰ筒状物の形状は、目的とするＦＲＰ製筒状体の形状に応じて円筒状や円錐台状に成形すればよい。またＦＲＰ筒状物の大きさは、目的とするＦＲＰ製筒状体の大きさにより適宜決められるが、通常直径６０cm～５m、長さ30cm～20m、厚さ２mm～２０mmとすることができる。ＦＲＰ筒状物は、タンクやサイロ等を設置する場所で製造する必要はなく、品質管理の行き届いた工場で製造すればよいので、その強度、耐薬品性、その他の性能が最良の状態のものを得ることが出来る。

ＦＲＰ筒状物をその母線方向に一条又は複数条切断してＦＲＰ板とするには、電動鋸、ジグソー等の工具を用いて行うことができる。切断されたＦＲＰ筒状物は比較的柔軟で、成形時に付与された曲率を変えることが可能であり、人力で容易にコイル状に巻き込んだり押し拡げて湾曲したＦＲＰ板とすることができる。そして幾層にも積み重ねることができるので効率よく輸送することができ、また設置場所で再び板状から筒状体とすることができる。

ＦＲＰ板を切断端部同士接合してＦＲＰ製筒状体を組み立てるには、端部同士を当接するか又は重ね合わせてその部分の両面をＦＲＰでオーバーレイして接合してもよく、切断端部同士を重ね合わせてボルト止め、鋲止め、接着剤による接着等の方法により接合してもよい。また接合する端部同士をＦＲＰ製や熱可塑性樹脂製の接合用部材を介して接合してもよい。切断端部同士を重ね合わせて接合する際には、その間にパッキングを挿入してもよい。このような接合方法により本発明の範囲が限定を受けるものではない。

以下図面に基づいて本発明を説明するが、図は本発明の具体的な実施の例を示すもので、本発明がこの図示例のみに限定されるものではない。

第１図はＦＲＰ筒状物(1)とその母線方向の切断線（Ａ—Ｂ）を示し、第２図はＦＲＰ筒状物(1)と母

線方向の4条の切断線（C−D、E−F、G−H及びJ−K）を示す。

第3図はFRP筒状物(1)を切断したのち押し拡げて湾曲したFRP板（1a）とし、このようなFRP板4枚（1a、1b、1c及び1d）を積み重ねた状態を示す。このようにして積み重ねることにより、効率よく輸送することができる。

第4図及び第5図はいずれも、FRP板（1a）の切断端部同士を接合して得られたFRP製筒状体の例を示すものである。第4図はFRP板（1a）の切断端部同士を重ね合わせ、ボルトとナットで接合した例である。第5図はFRP板（1a）の切断端部同士を当接してその当接部分の外側と内側の両面をFRP層（3a及び3b）でオーバーレイして接合した例を示す。また第6図は4枚のFRP板（1a、1b、1c及び1d）のそれぞれの間に4個の接合用部材（4a、4b、4c及び4d）を介在させ、そしてそれらをボルトとナットにより互いに接合してFRP製筒状体とした例を示すものである。

このように本発明に基づけば、強度及び耐薬品性に優れ、輸送効率にも優れた円筒型や角型の種々の大きさのFRP製筒状体が容易に得られるのである。

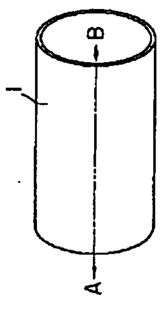
4. 図面の簡単な説明

第1図及び第2図はFRP筒状物とその母線方向の切断線を示す説明図であり、第3図はFRP板を積み重ねた状態を示す斜視図である。第4図、第5図及び第6図はいずれも本発明に基づくFRP製筒状体の例を示す見取図である。

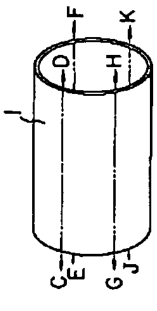
1 …… FRP筒状物
1a、1b、1c及び1d …… FRP板
2 …… ボルト・ナット
3a及び3b …… FRPオーバーレイ層
4a、4b、4c及び4d …… 接合用部材
5 …… ボルト・ナット

特許出願人　日本触媒化学工業株式会社
代理人　山口剛男

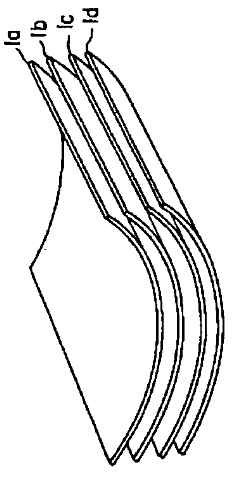
第1図



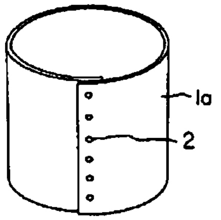
第2図



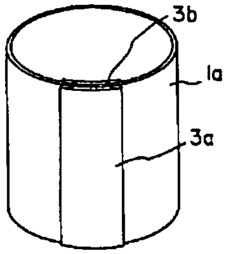
第3図



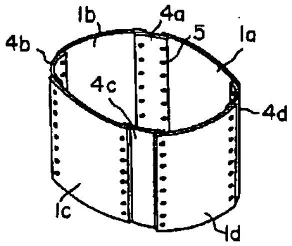
第 4 図



第 5 図



第 6 図



TRANSLATION

(19) JAPANESE PATENT OFFICE (JP)
(12) GAZETTE FOR EXAMINED PATENTS (B2)

(11) Patent Application Publication (Kokoku): **S57-22043**
(24)(44) Publication Date: May 11, 1982

Number of Inventions: 1 (Total of 4 Pages)

(51) Int. Cl.^{3}	Identification Code	(52) Internal File No.
C 08 F 14/26		7102-4J
2/00	104	
2/16		

(54) Title of the Invention:

MANUFACTURING METHOD FOR TETRAFLUOROETHYLENE WAX

(21) Application: S49-114892
(22) Application Date: October 5, 1974
(65) Patent Application Disclosure (Kokai): S51-41085
(43) Disclosure Date: April 6, 1976

(72) Inventor: Shozo FUMOTO
4-2-33, Yamate-cho, Suita-shi

(72) Inventor: Katsumi SHIMOFUKIKOSHI
1-17-8, Tsujine, Takatsuki-shi

(72) Inventor: Masafumi AKAMATSU
700 (illegible) Settsu-shi

(71) Applicant: Daikin Kogyo K.K.
Shin Hankyu Bldg.
1-12-39 Umeda, Kita-ku, Osaka

(74) Agent Attorney: Shigeru AOYAMA and one other

(57) CLAIMS

1 Manufacturing method for tetrafluoroethylene wax, characterized as using fluoroalkane or chlorofluoroalkane having 1 ~ 3 carbons in 5 ~ 90 mol% concentration toward total amount with tetrafluoroethylene as telogen, polymerizing tetrafluoroethylene in aqueous medium under pressure of 0 ~ 30 Kg/cm^{2}G and temperature conditions of 0 ~ 100°C.

DETAILED EXPLANATION OF THE INVENTION

This invention relates to manufacturing method for tetrafluoroethylene wax (hereinafter termed TFE), in particular, to industrially advantageous manufacturing method for chemically [and] thermally stable TFE wax.

Method of manufacturing wax by TFE telomerization has been known for a long time, and has been implemented industrially as well. However, many of the methods known in prior art were methods utilizing compounds undergoing telomerization as the reaction media; consequently, it was difficult to control reaction conditions such as temperature [and] there were problems with regulating molecular weight, etc. Methods using aqueous reaction media were also known, but there were problems such as inferior thermal stability of the product wax, [and] difficulties in separation of monomer and telomer after reaaction.

Method of forming low molecular weight by thermal decomposition of polytetrafluoroethylene (hereinafter termed PTFE) has also been known for a long time, but there are many disadvantages such as almost exclusive use of scraps because of the high cost of PTFE starting material, poor efficiency because of extremely low molecular weight substances generated as byproducts, difficulties in discharging highly toxic gases generated by thermal decomposition.

Further, as a recently developed method, there is the method of decomposition by irradiation of PTFE; with this, an improved method is also known, whereby irradiation with addition of oxygen and hydrogen effects efficient decomposition with a small amount of irradiation. However, irradiation generally needs special handling, and is high in cost; consequently, it is not utilized as a preferred industrial manufacturing method.

The inventors completed this invention as the result of conducting various studies to eliminate the defects of the aforementioned methods in prior art; by this means, it became possible to manufacture chemically and thermally stable TFE wax in an industrially advantageous way.

In other words, TFE wax has low molecular weight; in comparison to PTFE commonly used in molding, there is a far greater proportion of terminals rich in reactivity. Consequently, when TFE wax is mixed with other substances such as engineering plastics, heated and molded, end groups react with these materials, discoloration and other undesirable results frequently occur. In this invention, fluoroalkane or chlorofluoroalkane are used as telogen, as the result, end groups in the product TFE wax are chemically and thermally stable; the aforementioned defects seen in TFE wax heretofore are not found. For example, the ignition loss is usually 2% or less, in most cases, 0.5% or less.

Further, when telomerization was heretofore effected in aqueous medium, in order to increase economies, monomer (in other words TFE) and telogen were recovered together from the mixture, then separated into monomer and telogen; or without separation, provided for reuse by appropriate adjustment of concentration of the various components therein. Nonetheless, in the former case, when monomer is reused in reaction other than telomerization, telogen must be completely removed, a relatively large-scale purification unit becomes necessary. Further, in the latter case, there is much difficulty in keeping telogen concentration in the reaction vessel constant. However, when fluoroalkane or chlorofluoroalkane is used as telogen in this invention, mixture of monomer and telogen recovered from the reaction mixture can be separated by introduction into the purification process at the time of monomer manufacture, therefore, there is the advantage that a special unit need not be provided. In other words, TFE can be manufactured by the thermal decomposition of $CHClF_2$ as shown in the equation:

$$2CHClF_2 \rightarrow CF_2 = CF_2 + 2HCl$$

However, in this thermal decomposition mixture, in addition to TFE, a rather high proportion of $CHClF_2$ starting material is present; separation and purification are necessary. The objective of separation can be achieved by conveying the recovered gas comprising monomer and telogen from the aforementioned telomerization to this purification process. Further, in the aforementioned manufacture of TFE monomer by thermal decomposition of $CHClF_2$, some fluoroalkane and chlorofluoroalkane other than $CHClF_2$ are normally present from addition or substitution reaction toward starting material $CHClF_2$ and product TFE in the reaction mixture; therefore, even when fluoroalkane and chlorofluoroalkane other than $CHClF_2$ are used as telogen, in many cases, purification process identical to that in the aforementioned TFE manufacturing process can be utilized in separation of telogen and TFE monomer.

To implement the method of this invention, reaction is made to proceed by allowing TFE to come into contact with polymerization initiator in aqueous medium, and making adjustments during the reaction so that low molecular weight polymer is formed by action of telogen.

When telogen is not present, polymer having molecular weight of about $10^6 \sim 10^7$ is produced, but by the presence of telogen, polymer of lower molecular weight is produced. It is known that in general, polymer having molecular weight of about 10^5 is suitable for wax; so kind and weight of telogen are suitably selected to take this into consideration.

In the method of this invention, telogen is used in amount such that during the progress of the reaction, about 5 ~ 90 mol% concentration is maintained toward total amount with TFE; this varies with polymerization pressure, polymerization temperature, amount of decomposition of polymerization initiator, etc. Suitable polymerization pressure is about $0 \sim 30$ Kg/cm^2G, suitable polymerization temperature can be about 0 ~ 100°C.

As fluoroalkane and chlorofluoroalkane used as telogen in the method of this invention, $CHClF_2$, $CHCl_2F$, CH_2F_2, CHF_3, CCl_3F, CCl_2F_2, $CClF_3$, $CF_3 \cdot CHF_2$, $CCl_2F \cdot CCl_2F$, $CCl_2F \cdot CClF_2$, $CClF_2 \cdot CClF_2$, $CClF_2 \cdot CF_3$, $CF_3 \cdot CHF \cdot CF_3$ and the like can be listed as examples, in particular, $CHClF_2$ is preferred.

As polymerization catalyst, common catalyst such as ammonium persulfate is used. When there is mixing with other substances, e.g. engineering plastics, low reactivity of end groups is required. In particular, because wax has low molecular weight, and a large number of end groups, their effect on thermal stability cannot be ignored. From this standpoint, one recommended method is to use fluoro-peroxide that provides stable end groups as polymerization initiator. As example of such catalyst, di(chlorofluoroacyl)peroxide, for example, $(Cl(CF_2CFCl)_nCF_3COO)_2$ (n is integer 1 ~ 10), is cited in the specification in Japanese Patent Application Publication (Kokoku) Sho47-44031; by using this kind of polymerization initiator, it is possible to obtain wax having stable terminals, i.e. having low ignition loss, moreover, showing little reactivity toward other substances on mixing. However, there are problems in that handling of this peroxide is bothersome, moreover, it is very expensive.

When persulfate is used as polymerization initiator, particularly at high temperature, polymer terminal generated from catalyst becomes –COOH by the following reaction.

$$-(CF_2CF_2)_nSO_4 \xrightarrow{H_2O} -(CF_2CF_2)_nOH \xrightarrow{H_2O} -(CF_2CF_2)_{n-1}CF_2COOH + 2HF$$

This end group is thermally unstable and susceptible to decarboxylation. Thus

$$\alpha COOH = \frac{\text{Amount of persulfate decomposed in reaction (no. of moles)}}{\text{Product wax (no. of moles)}}$$

has a nearly proportional relationship to ignition loss; it was found that according to the measurement method below, in order to have ignition loss of 2.0% or less, αCOOH was 1.6 or less. However, amount of persulfate decomposition was obtained from calculations based on decomposition rate constant obtained from the following equation (here, R is gas constant, T is absolute temperature).

$$kd = 6.76 \times 10^{17} \exp(-32{,}200/RT)(\text{min.}^{-1})$$

Number of moles of product wax was obtained from calculations using average molecular weight obtained from melt viscosity by the following equation.

$$\overline{M} = 7.14 \times 10^3[\eta]^{0.2}$$

$[\eta]$: Melt viscosity at 380°C (poise)

Furthermore, as end groups in product wax molecules, in addition to those originating in aforementioned polymerization initiator, others are generated from telogen; when telogen is chlorodifluoromethane, end groups are formed when polymerization stops upon extraction of atom (mainly hydrogen) from this molecule by radical during polymerization and other end groups are formed when telogen from which atom has been extracted restarts polymerization; these end groups are unstable.

It is not particularly necessary to to add emulsifer, but it may be added to reduce the particle size of product polymer. As emulsisfier, ammonium salt of perfluoro- or ω-hydroperfluoro-alkylcarboxylic acid or alkali metal salt of sodium, potassium and the like are commonly used.

Separation of low molecular weight polymer product from the reaction mixture can be implemented by conventional methods. When reaction mixture is in the form of emulsion, polymer is made to coagulate by stirring, etc. As necessary, HNO_3 and the like may be added as coagulant. Separated polymer is washed with water to remove emulsifier and the like, dried to obtain wax in powder form.

Properties of the resultant wax and measurement methods are as follows.

Properties
Particle size range: 2 ~ 50 μ
Melt viscosity: $1 \times 10^4 \sim 1 \times 10^7$ poise
Ignition loss: 2% or less, in particular, 0.5% or less

Measurement methods of properties

Particle size range: Measurements were made with light transmission type particle size distribution measuring device Model SK (Seishin Co.). Measurements were made by transmitting light through liquid, where wax had been dispersed thoroughly in water by ultrasonic waves.

Melt viscosity: Measurements were made with high polymer type flow tester at shearing force of 0.457 Kg/cm^2 and temperature of 380°C. Test sample was packed in cylinder (i.d. 9.5 mm), heated to temperature of 380°C, extruded through orifice (i.d. 2.1 mm, length 8 mm); viscosity was obtained from extrusion rate at this time and expressed in units of poise.

Ignition loss: Test sample was placed in a platinum crucible, proportion of weight loss on heating for 1 hr at temperature of 300°C was measured and expressed in terms of %.

Next this invention is explained by citing practical examples.

Practical Example 1 ~ 7

Stainless steel polymerization vessel (total space 20 ℓ) was charged with water (10 part) that had been deionized and deoxygenated, sealed, thereafter air was discharged, telogen in amount shown in Table 1 and emulsifier in accordance with need were added. Next while TFE was added under pressure, temperature inside the vessel was adjusted to that listed in Table 1. Thereafter, amount of ammonium persulfate listed in Table 1 was added to initiate telomerization. Pressure drops when reaction starts, but pressure listed in Table 1 is maintained by further addition of TFE. After TFE (2 part) is consumed, TFE is removed from the vessel to end the reaction. When reaction products are in form of emulsion, stirring is continued to effect coagulation. Reaction products are separated, washed with water, thereafter dried to obtain powder in wax form.

In case of Practical Example 1 ~ 6, TFE monomer containing telogen, removed from the vessel at the end [of the reaction], is introduced into the purification process in the TFE manufacturing process by thermal decomposition of $CHClF_2$. In this case, thermal decomposition product of $CHClF_2$, in addition to TFE monomer, contains a large proportion of impurities of all kinds as well as unreacted $CHClF_2$; there are no problems when gas recovered after telomerization reaction, comprising mixture of TFE monomer and $CHClF_2$, is introduced.

Table 1 lists the yield of TFE wax obtained in this way and the results of property measurements, as well as the respective polymerization reaction conditions.

Table 1

Practical Example	1	2	3	4	5	6	7
Telogen	$CHClF_2$	$CHClF_2$	$CHClF_2$	$CHClF_2$	$CHClF_2$	$CHClF_2$	CH_2F_2
Amount of Telogen (gas concn %)	70	60	60	80	30	85	65
Polymerization Pressure (Kg/cm^2G)	6.5	2.5	2.5	4.5	4.5	4.5	6.5
Polymerization Temperature (°C)	80	60	90	80	80	40	80
Amount of Polymerization Initiator Used ($g/H_2O\ \ell$)	1.5	3	3	1.5	1.5	A N F*) 1.5 1.5 1.5	1.5
Emulsifier Concn (ppm)**)	300	100	100	–	–	–	300
Yield (Kg)	1.7	1.7	1.6	1.3	1.5	1.6	1.7
Particle Size (μ)	15	30	20	25	35	30	20
Melt Viscosity (10^4 poise)	62	500	51	40	600	200	40
Ignition Loss (%)	0.54	1.71	2.19	0.5	0.3	0.3	0.5

Note: *) A: $(NH_4)_2S_2O_8$, N: Na_2SO_3, F: $FeSO_4$

**) $C_7F_{15}COONH_4$

Transl: CR&D Language Solutions
CLEMENOR, LLC
December 12, 2003